DEVELOPMENT OF NANOFILTRATION FLAT SHEET MEMBRANE FOR BIOREFINERY APPLICATION

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ABSTRACT

In recent years, biorefining and bioenergy production have received considerable attention as an alternative way to renewable bioresources to produce similar energy and chemicals derived from fossil energy sources which represents a more sustainable path in the bioeconomy. Biomass residues available from forest, crops and agricultural processing are the main source for the production value added chemicals such as xylitol, ethanol, furfural and various sugars by acid-catalyzed hydrolysis. Hydrolyzed product normally contains mixture of sugar that needs to separate depending on the final target product. Several separation techniques can be used to separate the sugar component such as membrane based separation, chromatographic and molecular imprinting polymer. In the current study, nanofiltration (NF) flat sheet membranes were developed based on the different compositions of PES/NMP/PVP which are from 23 to 30 wt% PES. The membrane was tested for the separation of glucose, xylose and acetic acid. From the result obtained, acetic acid and glucose retentions were up to 90% while xylose retention up to 80%. Meanwhile, the separation factor of xylose to glucose was more than 1 for 28 wt% PES whiles the separation factor of acetic acid to xylose and glucose were less than 1 for 30 wt% PES.

ABSTRAK

Kebelakangan tahun ini, biorefining dan pengeluaran biotenaga telah mendapat perhatian sebagai kaedah alternatif kepada sumber biologi yang boleh diperbaharui untuk menghasilkan tenaga yang sama dan bahan kimia yang diperolehi daripada sumber-sumber tenaga fosil yang dipercahayai lebih sihat dalam Bioekonomi. Sisa biojisim yang didapati dari hutan, tanaman dan pemprosesan pertanian merupakan sumber utama bagi bahan kimia nilai pengeluaran tambah seperti xilitol, etanol, furfural dan pelbagai komponen gula dengan asid-bermangkin hidrolisis. Produk hydrolyzed biasanya mengandungi campuran komponen gula yang perlu dipisahkan bergantung kepada produk sasaran akhir. Beberapa teknik pemisahan boleh digunakan untuk memisahkan komponen gula seperti pemisahan berasaskan membran, kromatografi dan imprinting polimer molekul. Dalam kajian semasa, nanofiltration (NF) membran kepingan rata telah dikaji berdasarkan komposisi yang berbeza daripada PES / NMP / PVP yang 23-30% berat PES. Membran ini telah diuji untuk pemisahan glukosa, xylose dan asid asetik. Daripada keputusan yang diperolehi, asid asetik dan glukosa tahanan adalah setinggi 90% manakala pengekalan xylose setinggi 80%. Sementara itu, faktor pemisahan daripada xylose kepada glukosa adalah lebih daripada 1 untuk 28% berat PES manakala faktor pemisahan asid asetik untuk xylose dan glukosa yang kurang daripada 1 bagi 30% berat PES.

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LIST OF ABBREVIATIONS

R_{ace}	acetic acid retention
R_{glu}	glucose retention
R_{obs}	observed retention
R_{xyl}	xylose retention
X_{xyl}	xylose separation factor

Greek

α	separation factor

Subscripts

c	concentration
f	feed
i	i^{th} component
p	permeate
r	rententate

LIST OF ABBREVIATIONS

CFF	Cross flow filtration
DF	Diafiltration
MD	Membrane distillation
MF	Microfiltration
NF	Nonofiltration
NMP	N-methyl-2-pyrrolidone
PES	Polyethersulfone
PV	Pervaporation
PVP	Polyvinyl pyrrolidone
PWP	Pure water permeability
RI	Refractive index
RO	Reverse osmosis
SEM	Scanning electron microscope
UF	Ultrafiltration
UPLC	Ultra performance liquid chromatography
UV	Ultraviolent

1 INTRODUCTION

1.1 Motivation and statement of problem

The global economy has evolved within a paradigm reliant on fossil energy sources (coal, oil, natural gas) which provide the majority of the feedstock used to produce fuels and chemicals. However, the long-term utilization of these depletable resources is unsustainable due to their non-renewable nature and limited reservoirs (Uihlein and Schebek, 2009). Biomass represents an alternative source of chemical feedstock and energy, and biorefining biomass is analogous to petroleum refining (Octave and Thomas, 2009).

Biomass is a form of renewable energy, which widely used in the third world commonly. It is a term for all organic materials that stems from plants including algae, trees and crops. Green plants produce biomass through photosynthesis including all land- and water-based vegetation, and also all organic wastes (McKendry, 2002). The major components of the biomass are five sugars which are glucose, xylose, galactose, mannose, and arabinose, and four impurities which are sulfuric acid, acetic acid, hydroxymethyl furfural (HMF), and furfural (Xie *et al.,* 2005).

Bioethanol is one of the alternative energy resources that could partially replace gasoline and eliminate air pollution (Weng *et al.*, 2009). However, there are some steps of process need to be done to produce these alternative energy resources such as pre-treatments, hydrolysis of enzymatic, monosaccharides separation, microbial fermentation, etc. Acid hydrolysis was the major steps producing inhibitors such as acetic acid which limited the ethanol output of the fermentation process.

A number of specific membrane processes are of particular value for biorefining and bioenergy production: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), pervaporation (PV), membrane distillation (MD), and diafiltration (DF) (Hinkova *et al.,* 2002). The MF, UF and NF processes use porous membranes and are driven by hydrostatic pressure; PV uses nonporous membranes and is driven by a chemical potential gradient, while MD uses porous hydrophobic membranes and is driven by a thermal gradient (He *et al.,* 2012).

Nanofiltration is one of the known separation technique which presents a selectivity governed both by steric hindrance effects and electrostatic repulsions. It begins to be used in a wide range of applications in the food industry due to these interesting separation properties (Bouchoux *et al.*, 2005). Boussu *et al.*, (2008) have proved that NF is the best method for biorefinery production process as each type of technologies has its own advantages and limitations.

1.2 Objectives

The main objective of this research is to study the effect of polyethersulfone concentration during preparation of nanofiltration flat sheet membrane on the performance of biorefinery application.

1.3 Scope of this research

The following scopes of research are outlined to achieve the goal of the study:

i) To develop NF flat sheet membrane based on PES/NMP/PVP composition.

ii) To study the effect of PES concentration in the dope polymer solution from 23 to 30wt% on the performance of NF flat sheet membrane for glucose-xylose-acetic acid separation.

iii) To characterize the NF flat sheet membrane in term of pore structure and properties, water permeability and separation ability for glucose-xylose-acetic acid

1.4 Main contribution of this work

The main focus in this study is separation of monosaccharide and acetic acid impurities. Chromatographic method was the most common method for the sugar separation of glucose and xylose and impurity separation of acetic acid. Membrane based process such as reverse osmosis and nanofiltration had a potential for separating both sugar and the impurity. However, the used of them was limited and not thoroughly studied. Flat sheet membrane technology was widely applied for wastewater treatment and separation process nowadays. In this study, flat sheet membranes were produced to separate monosaccharides included glucose and xylose and the impurity acetic acid which were products of biomass processing.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the biomass processing in biorefinery, background of membrane, comparison between usage of different types of membrane, nanofiltration and selection of PES. A general description on the separation process concept is presented. This chapter also provides a brief discussion of the membrane types available for sugar separation, mentioning their applications and limitations for separation analysis. A summary of the previous experimental work on dope polymer solution preparation is also presented.

Chapter 3 gives a review of the chemicals used in dope polymer solution preparation by manipulating the concentration of PES on performances of flat sheet membrane. The performances of four different flat sheet membranes were compared with morphological pore structure size of flat sheet membrane, permeability water flux and rejection experimental data. The results and diagrams for permeability and rejection using formula, morphological structure of flat sheet membrane by Scanning Electron Microscope (SEM) and sugar separation analysis by Ultra Performance Liquid Chromatography is presented and compared with experiments.

Chapter 4 is devoted in testing the performance on different types of composition membrane being produced. A brief review of the morphological on pore structure is also presented. The separation process of sugar and acetic acid components by flat sheet membrane of different PES concentration is being studied and compared by determining from its separation efficiency through cross flow filtration. A detailed description of the water permeability testing is also outlined.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the descriptions of biorefinery applications, biomass processing, background of membrane, comparison of types of membranes, flat sheet membrane formation and parameter, sugar separation techniques with their properties and selection of polymer contents. A general description on the techniques used and their properties are presented. This paper will present the sugar separation with type of membrane used, chemical usages and production of flat sheet membranes.

2.2 Biomass processing in biorefinery

A biorefinery is defined as a manufacturing site involved in the refining of biomass material to yield purified materials and molecules. This conversion can be achieved using biological or thermochemical processing or a mixture of both. Downstream manufacturing sites processing materials/molecules from biomass are often termed secondary biorefineries. The concept of refining plant matter to yield energy, fuel and chemicals has been developed over several years and has now moved from theory through to demonstration and fully commercial manufacturing programmes. These production sites, designed to take plant matter and process it to energy, fuel and chemicals have been termed 'biorefineries' (The National Non-Food Crops Centre, 2007).

Biomass has been defined to be "any material, excluding fossil fuel, which was a living organism that can be used as a fuel either directly or after a conversion process" (ASTM 2002).Biomass consists of three main chemical elements which are carbon, hydrogen and oxygen. However, the other compounds such as nitrogen and also small quantities of other atoms, included alkali, alkaline earth and heavy metals can be found as well. Biomass is considered as a part of the carbon cycle where the carbon used to construct biomass was absorbed from the atmosphere as carbon dioxide by plant life during photosynthesis. Then, it will be recycled back to the air by combustion or decomposition. This cycle ensured that there is always a stable level of carbon in the atmosphere (BIOMASS Energy Centre, 2008). Table 2-1 indicates various source of the biomass.

Table 2-1: Sources of biomass

Biomass Resources Categories	Examples
Residues from primary biomass production	Wood from forestry thinning and felling residues; straw from a variety of cereal crops; other residues from food and industrial crops such as sugarcane, tea, coffee, rubber trees and oil and coconut palms
By-products and wastes from a variety of processes	Sawmill waste, manure, sewage sludge and organic fractions on municipal solid waste, used vegetable cooking oil
Dedicated plantations	Short rotation forestry crops such as eucalyptus and willow; perennial annual crops such as miscanthus; arable crops such as rapeseed and sugarcane

Biomass was a form of renewable energy, which widely used in the third world commonly. It was a term for all organic material that stems from plants (including algae, trees and crops). Green plants produced biomass through photosynthesis including all land- and water-based vegetation, and also all organic wastes (McKendry, 2002). The major components of the biomass were five sugars, glucose, xylose, galactose, mannose, and arabinose, and four impurities which weresulfuric acid, acetic acid, hydroxymethyl furfural (HMF), and furfural (Xie *et al*., 2005).

Biomass was one of the primary contributors to the world economy. It was a multiplex resource that be treated in multi ways directing to a variety of products. Moreover, it was also a source of a big variety of materials, electricity, chemicals and fuels. Corn refinery industry produced an open range of products including starch-based ethanol fuels for transportation today. The biomass industry produced additional ethanol by fermenting some by-product sugar streams (Chum & Overend, 2001). Biomass processing technologies interpreted value from biomass in various ways because biomass resources had different ratios of clearly variant molecular structures (Carbon, 2008). Any biological feedstock produced renewable energy which contained appreciable amounts of sugar or materials that be converted into sugar (Segneanu *et al*., 2013).

Cellulose and hemicellulose from plants and other biomass were hydrolyzed to produce sugars (i.e., glucose and xylose; see Figure 2-1). They served as a feedstock in fermentation to produce ethanol (as fuels), lactic acid, or other valuable chemicals once these sugars were separated from other impurities. The demand for producing fuels and chemicals from renewable biomass increased over the past decade. However, there was relatively high cost of producing fermentable sugars from biomass hydrolyzed using existing technology and was a major obstacle. The hydrolysis process of cellulose and hemicelluloses in biomass by sulphuric acid to sugars generated by-products (i.e., acetic acid) leaded to further degradation of the glucose to hydroxymethyl furfural (HMF) and the xylose to furfural. Moreover, various phenolic compounds were degraded from lignin and other compounds in biomass (Xie *et al.*， 2005).

These compounds were toxic to the downstream fermentation and limited the usefulness of the derived sugars severely when their concentrations exceeded threshold levels. Standard post hydrolysis process involved the neutralization of sulphuric acid, normally with lime (calcium hydroxide). A study by Wooley *et al*. showed that the limed hydrolyzate gave a low ethanol yield in fermentation test (20% of theoretical yield compared to 77% of theoretical yield from the fermentation of pure sugars). They showed that, an ion exclusion chromatography process was used to remove acids, as well as to isolate the sugars from the biomass hydrolyzate instead of adding lime *(Xie et al*., 2005).

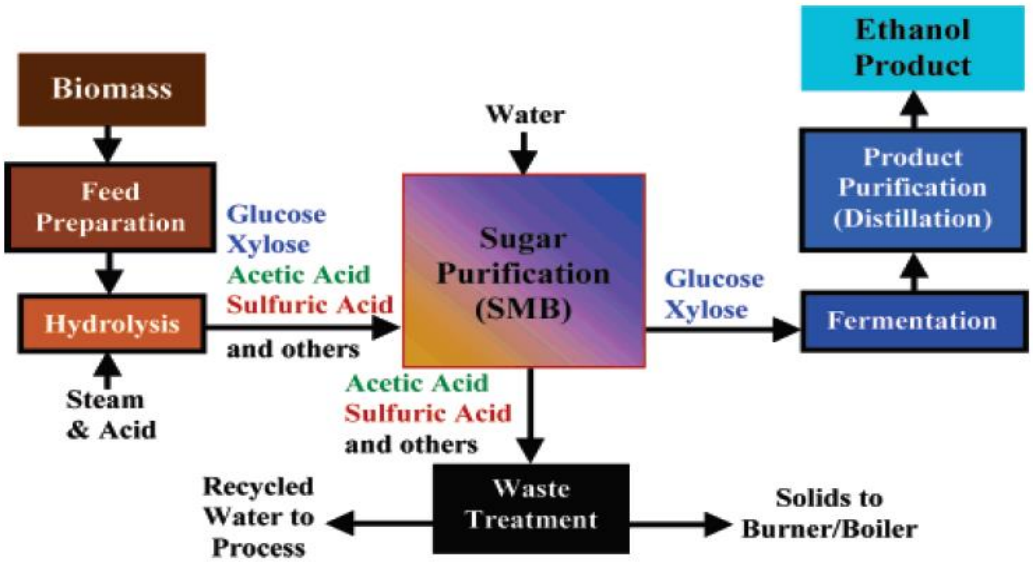

Figure 2-1: Schematic diagram of a simplified bioethanol production from biomass by Xie et al., 2005

2.3 Separation process

In early civilizations, separation process was developed include extraction of metals from ores, perfumes from flowers, dyes from plants, and potash from ashes of burnt plants; evaporation of sea water to obtain salt; refining of rock asphalt; and liquors distillation. Chemists used an analytical separation method called chromatography to determine the compositions of complex mixtures and preparative separation techniques for chemicals recovery (J.D. Seader *et al.*, 2011).

Figure 2-2 shows a general separation schematic of a separation process occurred. The feed and products may be vapor, liquid, or solid took place in one or more separation operations and the products might differ in phase and composition. However, if there is more than two species in the feed, the separation was not perfect and required more than two separation operations.

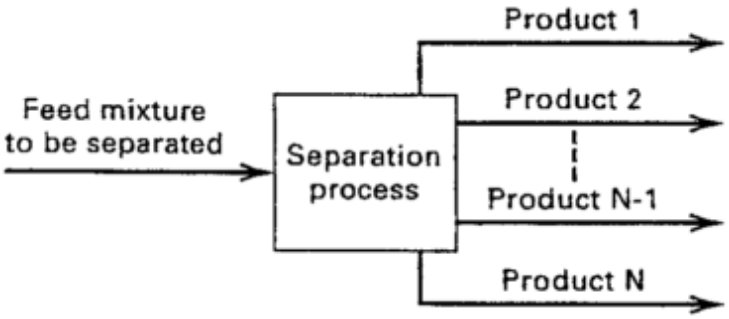

Figure 2-2: General separation process

The mixture components were induced to move into various separable spatial locations or phases by five basic separation methods in each separation operation as shown in Figure 2-3a was the most common separation techniques by creating a second phase, immiscible with the feed phase, by energy (heat and/or shaft-work) transfer or by pressure reduction such as distillation. A second technique which shown in Figure 2-3b by adding another fluid phase that absorbs, extracts, or strips certain species selectively from the feed such as liquid-liquid extraction. Separation by a barrier (shown in Figure 2-3c) was usually a polymer membrane that involved a gas or liquid feed and exploited differences in species permeabilities through the barrier which was less common but of growing importance currently as well as shown in Figure 2-3d. The agent consisted of particles that were porous to achieve a high surface area, and differences in species adsorbability were exploited. Lastly, external fields (centrifugal, thermal, electrical, flow, etc.), shown in Figure 2-3e, were applied in specialized cases to liquid or gas

feeds, with electrophoresis being especially useful for proteins separation by exploiting differences in electric charge and diffusivity (J.D. Seader *et al.*, 2011).

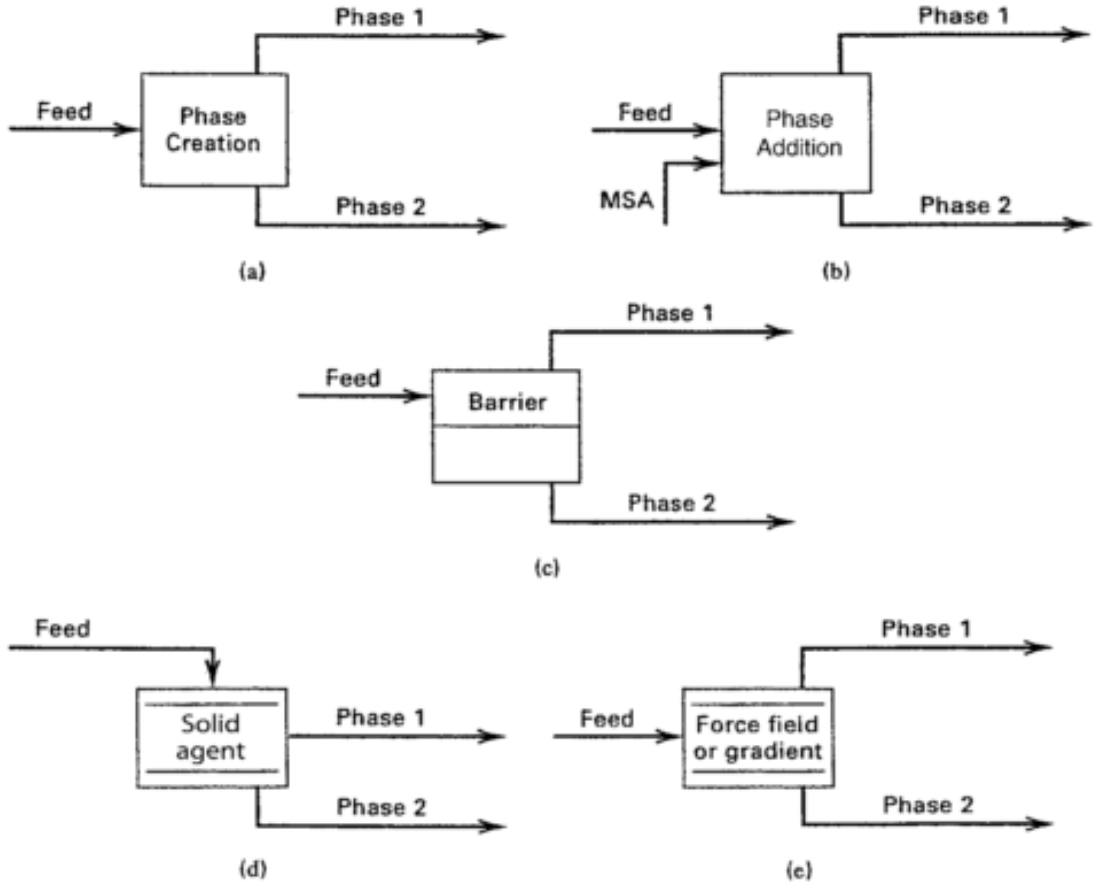

Figure 2-3: Basic separation techniques: (a) separation by phase creation; (b) separation by phase addition; (c) separation by barrier; (d) separation by solid agent; (e) separation by force field or gradient

Some separation process can be classified in terms of the physical or chemical properties of the components which were to be separated indicated in table below. From the table, membrane separation was facilitated by differences in the size, vapour pressure, affinity, charge, density or chemical nature of molecules. The number of possible separation principles, some of which were used in combination, distinguish this technique from other separation processes and also provided an indication of the number of situations in which membrane processes can be applied (Mulder, 1997).

Table 2-2: Separation process based on physical/chemical properties

Physical/Chemical Properties	Separation Process
Size	Filtration, microfiltration, ultrafiltration, dialysis, gas separation, gel permeation chromatography
Vapour pressure	Distillation, membrane distillation
Freezing point	Crystallization
Affinity	Extraction, adsorption, absorption, reverse osmosis, gas separation, pervaporation, affinity chromatography
Charge	Ion exchange, electrodialysis, elec1rophoresis, diffusion dialysis
Density	Centrifugation
Chemical nature	Complexation, carrier mediated transport

2.4 Background of membrane

Membrane technology has become a dignified separation technology over the past decennia. In 40 years ago, a simple concept introduced a range of separation methods: a membrane to supplement or replace several individual techniques such as distillation, adsorption, extraction, crystallization, etc. Membrane filtration was an economical way and very efficient of separating components that were suspended or dissolved in a liquid (Spring & Hashsham, 2006). Membrane filtration can be used as an alternative for flocculation, sediment purification techniques, adsorption (sand filters and active carbon filters, ion exchangers), extraction and distillation (Lenntech, 1998).

A membrane is a permeable or semi-permeable phase, usually a thin polymeric solid, which governed the motion of certain species. This added phase was acted as a barrier between the feed and the product stream for separation purpose. As with all separations, it gave one product in which certain components were in low concentrations and a second product in which these components were in high concentrations by controlling the relative transport rates of different species through it. There are two simple factors can define the performance of the membrane: productivity (flux) and selectivity (retention or separation factor) (Bhattacharya, 2013). Selectivity and productivity are membrane-dependent.

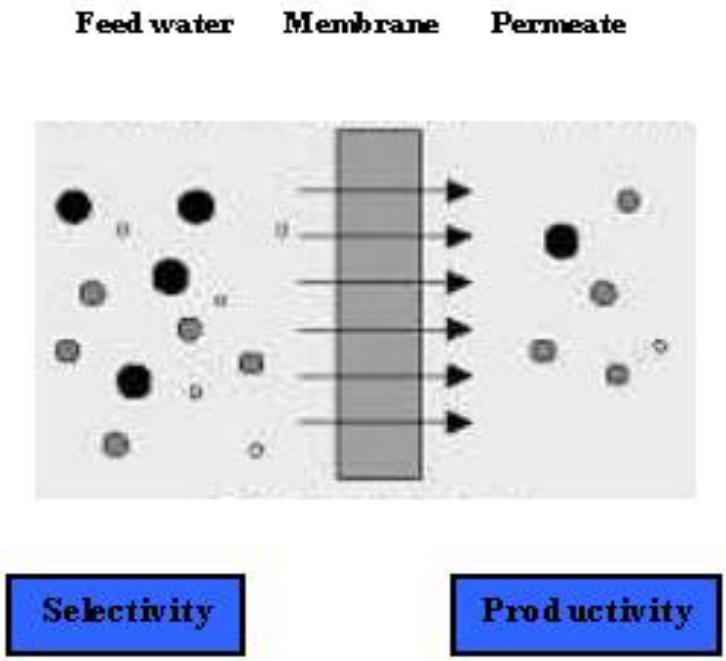

Figure 2-4: Selectivity and productivity of a membrane (Lenntech, 1998)

The common feature of the achievement of separation for all membrane processes was via a membrane. The membrane acted as a permselective barrier between two homogeneous phases. Due to increasingly important of separations using membrane in the industrial process, the membranes had evolved from laboratory tools to industrial products with commercial effect and significant technical. The membrane used in which processes were classified based on the driving force used in the process as shown in

Table 2-3 (Bhattacharya, 2013).

Transport through the membrane took place when the components in the feed were applied by a driving force. The driving force was a pressure difference or a concentration (or activity) difference across the membrane in most the membrane processes. Parameters such as pressure, concentration (or activity) and even temperature may be included in one parameter, the chemical potential μ. Another driving force in

membrane separations was the electrical potential difference. This driving force only influenced the transport of charged particles or molecules (Mulder, 1997).

Table 2-3: Classification of membrane processes according to their driving forces

pressure difference	concentration (activiry) difference	temperature difference	electrical potential difference
microfiltration	pervaporation	thermo-osmosis	electrodialysis
ultrafiltration	gas separation	membrane	electro-osmosis
nanofiltration	vapour permeation	distillation	membrane
reverse osmosis	dialysis		electrolysis
piezodialysis	diffusion dialysis		
	carrier-mediated transport		

Different pressure-driven membrane processes can be used to concentrate or purify a dilute (aqueous or non-aqueous) solution. The characteristics of these processes were the continuous phase of the solvent and low concentration of the solute. The panicle or molecular size and chemical properties of the solute determined the structure, i.e. pore size and pore size distribution, necessary for the membrane employed. Various processes can be distinguished related to the particle size of the solute and consequently to membrane structure such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The principle of the four processes is illustrated in figure below:

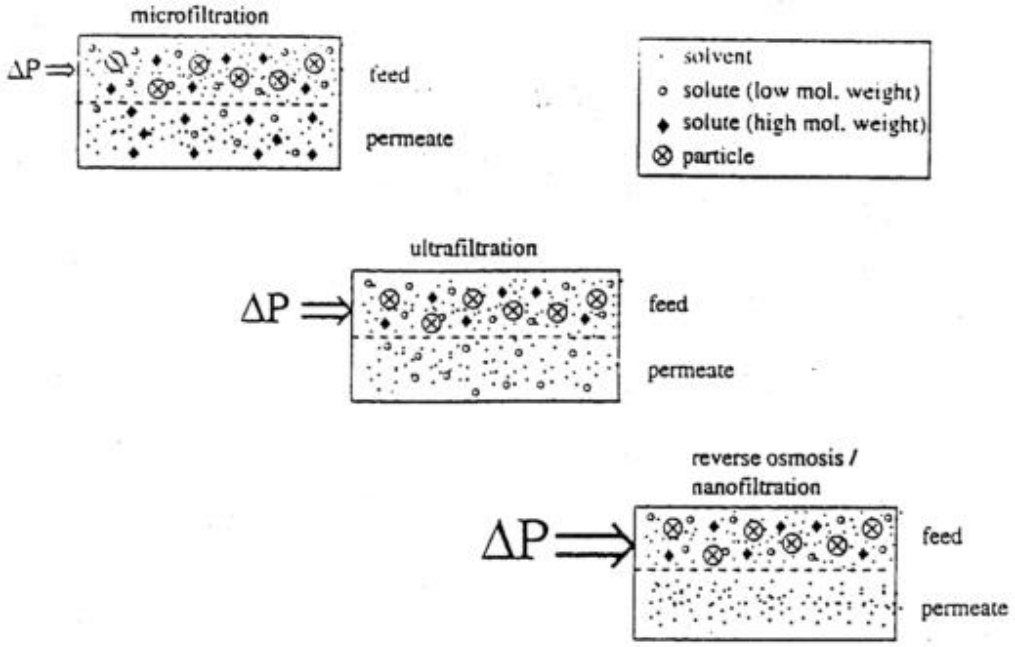

Figure 2-5: Schematic representation of micro filtration, ultrafiltration, nanotiltration and reverse osmosis

MF and UF were used for the removal of larger particles due to their open characteristic with high productivity and low pressure differences. For smaller particles such as salts removal from the water, NF and RO were applied. However, NF and RO did not work according to the pores principle and this caused separation took place by diffusion through the membrane. Higher pressure was required to perform NF and RO than UF and MF with lower productivity (Lenntech, 1998).

Table 2-4: Pressure driven membrane processes (M.H.V. Mulder, 1996)

Membrane Process	Typical Pressure (bar)	Typical permeability ($l/(m^2.h.bar)$)	Morpholoy of selective layer
Microfiltration	0.1-2	>50	Porous
Ultrafiltration	1-5	10-50	Porous
Nanofiltration	5-20	1.4-12	Porous/ Dense
Reverse Osmosis	10-100	0.05-1.4	Dense

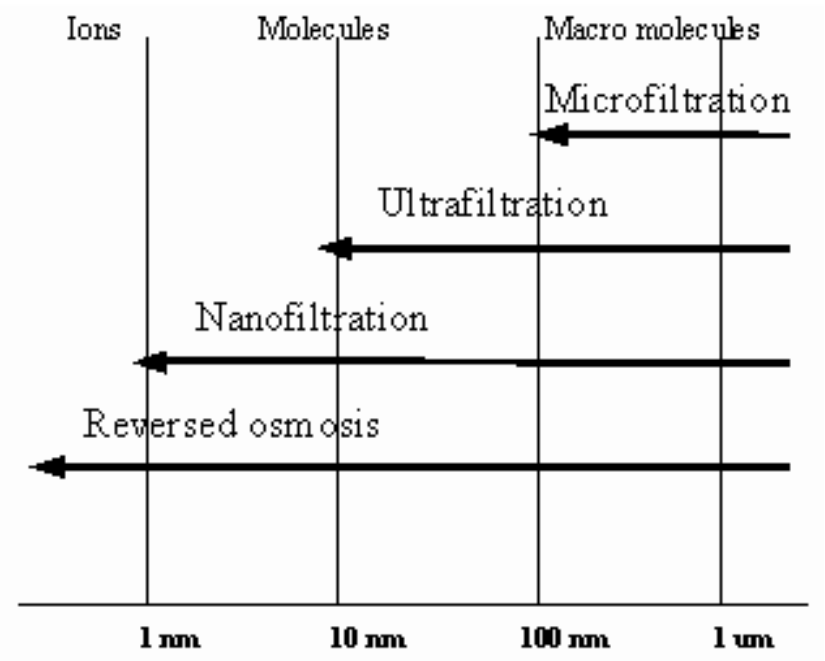

Figure 2-6: Classification of membrane fitration (Lenntech, 1998)

2.5 Comparison of ultrafiltration, nanofiltration and reverse osmosis

Filtration is a removal process of particulate matter from water by forcing the water through a porous media whether naturally such as in the case of sand, gravel and clay, or a membrane wall made of various materials (SDWF, 2014).

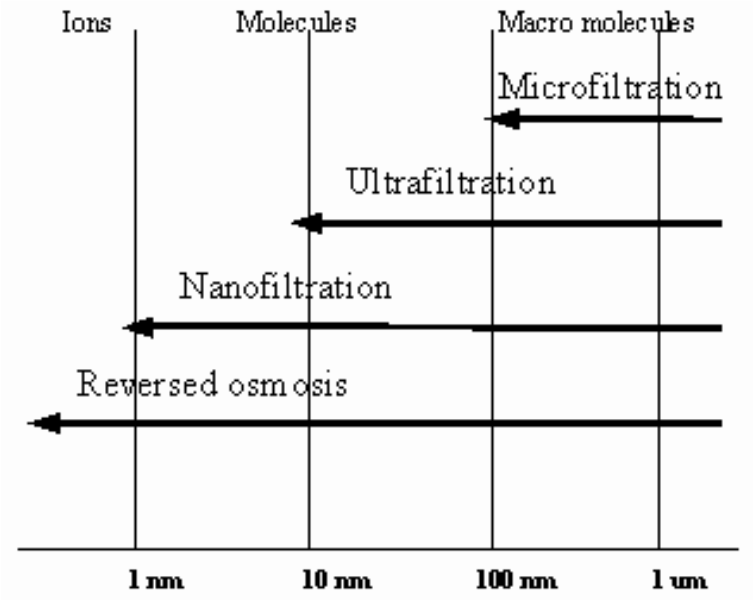

Figure 2-7: Classification of membrane fitration (Lenntech, 1998)

Ultrafiltration was a membrane process whose nature lied between microfiltration and nanofiltration that had a pore size ranged around 0.01 μm to 1nm. It was used to retain macromolecules and colloids from a solution typically. Ultrafiltration involved in similar membrane processes as microfiltration based on the same separation principle. However, ultrafiltration membranes had an asymmetric structure with a much denser top layer (smaller pore size and lower surface porosity) and consequently a much higher hydrodynamic resistance compared to microfiltration (Mulder, 1997).

Reverse osmosis and nanofiltration were used when small organic molecules such as glucose and sucrose or low molecular weight solutes such as inorganic salts have to be separated from a solvent. Both processes were considered as one process since they had the same basic principles but their differences will be emphasized in table below.

A nanofiltration filter has a pore size around 0.001μm. Nanofiltration removed nearly all viruses, most organic molecules and a range of salts. Nanofiltration was often used to soften hard water as it removed divalent ions that caused harden of water (SDWF, 2014).

In reverse osmosis or sometimes called hyperfitration, the membrane had to be permeable to the solvent, water and impermeable to solutes and pressure-drive used so that the water through the membrane. The name reverse osmosis arised from the fact that the direction of solvent flow is the reverse to that occurring in osmosis, as illustrated in Figure 2-8. This process was widely studied in desalting brackish or sea water (Sammon, 1974). Reverse osmosis filters have a pore size around 0.0001μm. Reverse osmosis commonly used in water desalination as it removed monovalent ions in the water. After water passes through a reverse osmosis filter, it is essentially pure water.

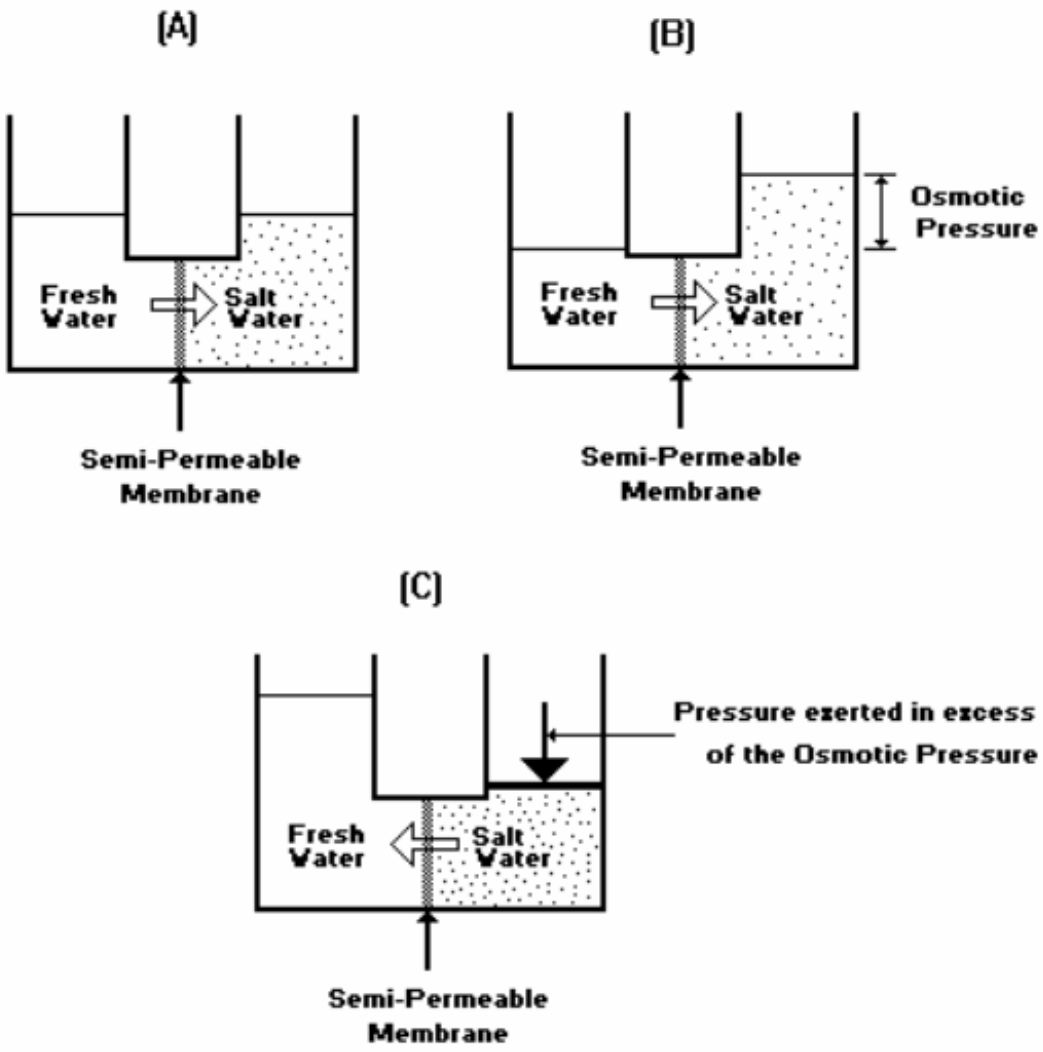

Figure 2-8: Osmosis and reverse osmosis

Table 2-5: Summary of nanofilrration and reverse osmosis

	Nanofiltration	Reverse Osmosis
Membranes	Composite	Asynunetric or composite
Thickness	Sublayer ≈ 150 µm	Sublayer ≈ 150 µm
	Toplayer ≈ 1 µm	Toplayer ≈1 µm
Pore size	<2 nm	<2 nm
Driving force	Pressure (10 - 25 bar)	Pressure:
		brackish water 15- 25 bar